

PATENT ABSTRACTS OF JAPAN

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(54) ROOM TEMPERATURE CURING COMPOSITION AND ITS PRODUCTION

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain the subject composition having sufficiently low viscosity, free from the loss of the flexibility of a cured material even in the case of using an inorganic filler and useful as a sealing material, etc., by mixing plural specific high molecular polymers having different molecular weights.

SOLUTION: (A) 100 pts.wt. of a high molecular weight polymer having a molecular weight of 8000-30000 in which $\geq 50\%$ total molecular terminal groups are hydrolyzable silicon-containing groups is compounded with (B) 1-200 pts.wt. a high molecular weight polymer of 4000-30000 in which $< 50\%$ total molecular terminal groups are hydrolyzable silicon-containing groups. Further, it is preferable that both the main chains of the component A and the component B are substantially polyethers and both the hydrolyzable silicon-containing groups of the component A and the component B be expressed by the formula R_2SiXaR_{13-a} [R1 is a 1-20C (substituted) monovalent organic group; R2 is a divalent organic group; X is OH or a hydrolyzable group; (a)=1-3]. Furthermore, preferably, (C) a plasticizer, especially free from a low molecular plasticizer, is contained or a plasticizer is not substantially contained.

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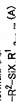
CLAIMS

[Claim (a)]

[Claim 1] Polymer (I) of the molecular weights 8000-30000 whose not less than 50% of all the molecular terminal groups are hydrolytic silicon groups. And a room-temperature-curing nature constituent in which less than 50% of all the molecular terminal groups contain one to polymer (II) 200 weight section of the molecular weights 4000-30000 which are hydrolytic silicon groups to polymer (I) 100 weight section.

[Claim 2] A room-temperature-curing nature constituent of Claim 1 whose both main chain of polymer (I) and main chain of polymer (II) are polyether intrinsically.

[Claim 3] Polymer (I) — a room-temperature-curing nature constituent of Claim 1 by which both a hydrolytic silicon group and a hydrolytic silicon group of polymer (II) are expressed with a following formula (A).



R^1 is a univalent organic group substitution of the carbon numbers 1-20, or unsubstituted among a formula, R^2 is a divalent organic group, X is a hydroxyl group or a hydrolytic basis, and a is an integer of 1-3.

[Claim 4] Claim 1, a room-temperature-curing nature constituent of 2 or 3 in which a room-temperature-curing nature constituent does not contain a plasticizer substantially.

[Claim 5] Claim 1, a room-temperature-curing nature constituent of 2 or 3 which a room-temperature-curing nature constituent contains a plasticizer further, and do not contain a low molecule plasticizer as the plasticizer.

[Claim 6] As opposed to polymer (I) 100 weight section of the molecular weights 8000-30000 whose not less than 50% of all the molecular terminal groups are hydrolytic silicon groups. A manufacturing method of a room-temperature-curing nature constituent, wherein less than 50% of all the molecular terminal groups mix one to polymer (II) 200 weight section of the molecular weights 4000-30000 which are hydrolytic silicon groups.

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001] [Field of the Invention] This invention relates to the room-temperature-curing nature constituent hardened under hygroscopic-surface-moisture existence.

[0002] [Description of the Prior Art] The method of making harden various kinds of polymers which have a hydroxylic silicon group, and using it for a sealing material, adhesives, etc. is known well, and is a useful method industrially.

[0003] The polymer especially whose main chain is polyether among such compounds is liquified at a room temperature, and when a hardened material holds pliability also at low temperature comparatively and uses for a sealing material, adhesives, etc. it is provided with the desirable characteristic.

[0004] As a polymer of such hygroscopic-surface-moisture hardenability, the polymer of the hygroscopic-surface-moisture pliability which has a hydroxylic silicon group is mentioned to the prior art, for example, JP-5-72827A, JP-3-47825A, etc. In the polymer which has a hydroxylic silicon group, the pliability is improved, although the pliability of a hardened material increases, the viscosity of a polymer becomes high and workability gets remarkably bad, so that the molecular weight is generally low.

[0005] When the molecular weight of such a polymer is small, although viscosity becomes low, a hardened material is inferior to pliability. In order to make a polymer into hypoviscosity, maintaining the pliability of a hardened material until now, various kinds of plasticizers have been used.

[0006] As such a plasticizer, aromatic carboxylic acid ester, aliphatic-carboxylic-acid ester species, alcohol ester, phosphoric ester, an epoxy plasticizer, a chlorinated paraffin, etc. are used. However, since these plasticizers are translatable, when it is used for a sealing material, etc., there is a fault which has the surface contamination after contamination and paint of the celling part circumference and an adverse effect to an adhesive property.

[0007] The hardenability constituent which did not reduce the pliability of the hardened material and added the very low reactant plasticizer of transatability was proposed by JP-5-59267A to the polymer of the hygroscopic-surface-moisture hardenability which has a hydroxylic silicon group in order to cancel such a fault. However, in the use to a sealing material, etc. when pliability is higher, it has the good characteristic of elongation and it parts on the surface, the hardenability constituent in which surface stain resistance has been improved is called for. Although various kinds of inorganic bulking agents are usually used in combination called a actual sealing material and others, a polymer's own pliability is much more required for use of a bulking agent in order to harden the physical properties of a hardened material.

[0008] As a polymer of such hygroscopic-surface-moisture hardenability, the polymer of the hygroscopic-surface-moisture pliability which has a hydroxylic silicon group is mentioned to the prior art, for example, JP-1-279858A. It is mixed from such a viewpoint to a hydroxylic silicon group content, polyether polymer, and the constituent which does not contain plasticizers, such as decyl phthalate, is indicated, however, when the addition of the terminal unsaturated group content polyether compound lowered, the polymer which does not have a crosslinking group at all oozed out on the surface gradually after hardening, and especially the hardened material of such a constituent had a fault the hardened material surface comes to be alkali of a fault all over.

[0009] Although the constituent which blends the narrow hydroxylic silicon group content polyether polymer of molecular weight distribution without a plasticizer was indicated to JP-5-45403A, even if

it did not use as a plasticizer, it had practical viscosity, and when a hardened material was flexible, it had a fault to which hardening becomes very slow.

[0010] The example which furthermore mixes and uses two or more sorts of hydroxylic silicon group content polyether polymers in which the number of branching differs for JP-5-63403A to JP-5-65404A. The example which mixes and uses two or more sorts of hydroxylic silicon group content polyether polymers in which molecular weight distribution differs is shown. However, since there are more rates of the hydroxylic silicon group in all the molecular terminal groups of the polyether polymer which at mix than 50%, when especially inorganic bulking agent such as silicon carbonate, [0011] and there is a fault applied to the pliability of a hardened material without a plasticizer.

[Problem] to be Solved by the Invention Then, even if the viscosity of the constituent could be satisfied practically and used the inorganic bulking agent, the hardened material was flexible, the extension characteristic of the hardened material was good, and as a result of examining the constituent which does not pollute a surface coat, it resulted in this invention.

[0012] [Means for Solving the Problem] That is, this invention is the following invention. As opposed to polymer (0) [of the molecular weights 9000~30000], and polymer (1) (00 weight section whose not less than 50% of all the molecular terminal groups are hydroxylic silicon groups, A room-temperature-curing nature constituent in which less than 50% of all the molecular terminal groups contain one polymer (0) (200 weight section of the molecular weights 4000~30000) which are hydroxylic silicon groups, And a manufacturing method of a room-temperature-curing nature constituent characterized by making one to polymer (0) (200 weight section to polymer (1) (00 weight section).

[0013] [Embodiment of the Invention] As for both polymer (0) and polymer (1) that are used by this invention, consisting of polymer intrinsically is the main chain of a molecule (1) preferred.

[0014] As for such a polymer, what is obtained by introducing a hydroxylic silicon group by the suitable method for a polyether containing hydroxylic silicon group is preferred. For example, JP-5-72827A, JP-3-47825A, JP-5-72827A, JP-3-78627A, JP-46-30711B, JP-48-38311B, JP-46-11559B, etc. can be examples.

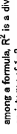
[0015] A polymer containing hydroxylic group is obtained by polymerizing monoeopide, such as butanediol, ethylene oxide, and an ester, and an ester.

[0016] The compound which has 2~10 active hydrogen as an initiator is preferred. A polyhydroxy compound is preferred and the polyhydroxy compound which has 2~4 hydroxyl groups especially is preferred. Specifically Ethylene Glycol, a diethylene glycol, propylene glycol, Dipropylene glycol, neopentyl glycol, 1,4-butanediol. There is polyol of low molecular weight from the object produced by making monoeopide react to 1,8-hexanediol, glycerin, trimethylolpropane, pentaerythritol, diglycerol, a shock alcohol, and these. One-sort single use or two or more sorts of concomitant use may be sufficient as these. An unsaturation group content mono- hydroxy compound like allyl alcohol can also be used.

[0017] As monoeopide, there are propylene oxide, butylene oxide, ethylene oxide, allyl glycidyl ether, etc. Especially propylene oxide is preferred. As a catalyst, catalysts such as an alkaline metal catalyst, a composite metal cyanide complex catalyst, and metalloporphyrin, are mentioned.

[0018] Especially desirable polyethers containing hydroxylic group are polyoxypropylene diol, polyoxypropylene triol, polyoxypropylene tetraol, and polyoxypropylene hexaol. When using for following (1) or the method of (4), polyether of olefin ends, such as polyoxypropylene glycol monoallyl ether, can also be used.

[0019] The hydroxylic silicon group should just be a silicon group with which hydroxylic and unsaturated groups are bonded with the silicon surface moisture. The silicon content group which has the hydroxylic group is bonded directly with the silicon atom can be used. For example, the basis compound with a formula (A) is preferred.



[0022] R¹ is a univalent organic group the substitution of the carbon numbers 1~20, or unsubstituted among a formula, R² is a divalent organic group, X is a hydroxyl group or a hydroxylic basis, and a is an integer of 1~3.

[0073] Working examples 1-6 and comparative examples [polymer (I), polymer (II) (or polymer for comparison) or them, and dioctyl phthalate (DOP)] in Table 1-2, mixed linear were obtained and the viscosity (unit: cP) at the 25 °C was measured.

[illegible]

[0075] (1) 50% modulus (unit: kg/cm²), breaking strength (unit: kg/cm²), and after being extended (unit: %) and using mixture as a sheet about 2 mm thick. After carrying out cure for seven days at 50 °C, moisture does not mix, and was measured about what was pierced with the JIS No. 3 needle immediately for seven days at 70 °C, it was measured about what was pierced with the JIS No. 3 needle.

[0076](2) Hardenability : the hardenability after 6-hour neglect was judged for the mixture by finger touch under the condition of 20 °* and 65RH. It was assumed that that from which O is a tuck freeler in evaluation, and x are not a tuck freeler.

[0077] (3) Pliability of a hardened material: the pliability of the hardened material in which carried out the curing reaction of the mixture of the hardened material and the curing agent was evaluated. The cure of this mixture and it was obtained was also evaluated. Or [that x which has pliability desirable as a sealing material for construction is too hard as a sealing material for construction] — or, it was presupposed that it is too soft.

[0078](4) Aging: there is no bleed out, such as an unrescued material, in the surface after two-week neglect at 50 °w, or the unpainted hardened material surface was examined by finger touch. O As for what bleed out was not accepted to, and y bleed out should be accepted.

[0079] (3) Stain resistance of a paint surface: After painting a solvent system allyl paint (the Rock Paint Co., Ltd. make, house paint) to what was stiffened as a 1-mm thickness sheet, and one month after being exposed to the outdoors after one-week heating at 70 °C, the dirt situation of the paint surface was observed. Q Although dirt had adhered a little, a beautiful thing and x assumed that adhesion of dust etc. is remarkable and dirty.

ation to cases etc. is remarkable and only [000] the case. The comparative example 2, the comparative example 0 (here polymer (II) is not used), reveals in which a hardened material is too hard and it is desirable as a sealing material cannot be placed as a talis shows. A paint film surface is made to polute with the compound which used the invention as a talis shows. A paint film surface is made to polute with the compound which used the invention as a talis shows. A paint film surface is made to polute with the compound which used the invention as a talis shows.

Table 17

Table 17

実施例	1	2	3	4	5	6
a	70	70	70	70		
b					100	
c	30	30	30	30		100
d	60					
e		60				
f			60			
g				60		
h					60	
i						60
j						
k						
粘度	1200	900	900	1000	700	1000
50℃モジュラス	1.0	1.1	1.3	0.9	1.8	1.7
軟化温度	5.8	6.0	6.4	5.6	7.9	8.2
伸び	830	810	790	830	750	850
酸化性	○	○	○	○	○	○
炭化物の生成性	○	○	○	○	○	○
熱安定性	○	○	○	○	○	○
機械安定性	○	○	○	○	○	○

[0082]

[Table 2]

比較例	1	2	3	4	5	6
a	70		70	112		
b	30		30	48		
c		160				
d						80
e						80
f						80
g					160	
h						
i						
j						
k						
l						
m	60					
n						
o						
p						
q						
r						
s						
t						
u						
v						
w						
x						
y						
z						
DOP			60			
粘度	960	300	3300	1200	1060	7100
50℃モジュラス	0.8	4.2	2.0	3.0	0.4	4.0
溶解性	5.8	9.5	8.0	8.5	2.5	9.0
熱安定性	820	480	750	720	950	520
耐水性	○	○	○	○	×	×
炭化傾向・炭化率	○	○	○	○	○	○
耐酸化性	○	○	○	○	○	○
耐熱安定性	○	○	○	○	○	○
耐熱劣化	○	○	○	○	○	○
耐熱劣化の特性値	○	○	○	○	○	○

[0083]

[Effect of the Invention] Even if the room-temperature-curing nature constituent of this invention has low viscosity enough and it uses an inorganic bulking agent, it has the effect of not reducing the pillability of a hardened material. When the constituent of this invention is used for a sealing material etc., it does not have contamination or the adverse effect to an adhesive property of the ceiling part circumference or a paint surface.

[Translation done.]

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various denaturation amines used as a hardening agent of an epoxy resin.

[Amendment 7]

[Document to be Amended]Des

Item(s) to be Amended 10052

[Method of Amendment]

[Proposed Amendment]

[0025] It is considered as a bulking agent, the publicly known following bulking agent can be used. The calcium carbonate which carried out the surface treatment of the surface with fatty acid or a resin acid system organic matter, Colloid calcium carbonate with a mean particle diameter of 1 micrometer or less which furthermore impalpable powder—had this, Calcium carbonate, such as precipitated calcium carbonate with a mean particle diameter of 1–3 micrometers manufactured with a sedimentation method, and heavy calcium carbonate with a mean particle diameter of 1–20 micrometers. Fumed silica, sedimentation nature silica, a silicic acid anhydride, hydrous silicic acids, carbon black, Magnesium carbonate, diatomite, calcination clay, clay, titanium oxide, Powder state bulking agents, such as bentonite, organic bentonite, ferric oxide, a zinc oxide, an active white, a white titanium, wood flour, pulp, a cotton cloth, a cotton cloth shell flour, chaff powder, graphite, aluminum impalpable powder, and the First powder. And the Second powder, such as glass filler, a glass filament, carbon fiber, the Kevlar, the textile, and a polyethylene fiber.

Amendment 87

[Document to be Amended]

[Item(s) to be Amended] 10054

[Method of Amendment]Change

[Proposed Amendment]

[Ox]Ox is fully hypoviscosity can be used, although the room-temperature-curing nature constituent in this invention is fully hypoviscosity in itself and it is preferred not to use a plasticizer substantially. As a plasticizer, for example Diethyl phthalate, Phthalic acid alkyl ester, Phthalic acid diethyl ester, Phthalic acid benzyl ester, Diethyl phthalate, Aliphatic-carboxylic-alkyl alkyl ester, pentaerythritol ester, such as succinic acid diisobutyl, diisobutyl sebacate, and butyl oleate etc. Triethyl phosphite, Phosphoric ester, such as triethyl phosphite, epoxy plasticizer, chlorinated paraffin, such as chlorinated soybean oil and epoxy stearic acid benzyl, etc. can be independent, or can use it, with two or more sorts of mixtures.

[Amendment 9]

[Document to be Amended] Description

Item(s) to be Amended 10055

[Method of Amendment]Change

[Proposed Amendment]

[0055] However, a low molecule plasticizer has a problem this invention tends to carry out (a problem) after [room-temperature-curing nature constituent hardening] bleed out among such plasticizers, and it is preferred not to use it. That is, it is preferred for the room-temperature-curing nature constituent of this invention to contain a plasticizer further, and not to contain a low molecule plasticizer as the plasticizer. The compound itself is low molecular weight, and a low molecule plasticizer refers to the plasticizer which does not have a reactant group. For example, it is phthalic acid alkyl ester.

[Amendment 10]

[Document to be Amended]Description

Item(s) to be Amended 0083

[Method of Amendment] Change

[Proposed Amendment]

[0093] Effect of the Invention] Even if the room-temperature-curing nature constituent of this invention has low viscosity enough and it uses an inorganic bulking agent, it has the effect of not reducing the pliability of a hardened material. When the constituent of this invention is used for a sealing material etc., it does not have contamination or the adverse effect to an adhesive property of the ceiling part circumference or a paint surface.